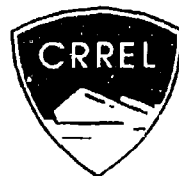AD-A286 374

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Softening of Rigid PVC by Aqueous Solutions of Organic Solvents

Louise V. Parker and Thomas A. Ranney

August 1994

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Abstract

This research examined softening of rigid PVC by aqueous solutions of organic solvents known to be good PVC swelling agents. Significant changes in the hardness readings of rigid PVC exposed to aqueous solutions of methylene chloride (a good PVC swelling agent) occurred at thermodynamic activities as low as 0.1, which is much lower than has been reported or predicted. Rigid PVC became rubbery after exposure to 0.6 activity solutions of methylene chloride. Whether a similar phenomenon occurs with TCE, which is not as good a PVC swelling agent, is not clear from these preliminary studies. This study also looked at the effect of a mixture of several organic solvents dissolved in an aqueous solution. A solution that contained three good PVC swelling agents each at an activity of 0.3 rapidly softened PVC (within 2 days). This indicates that there is some type of interactive or cumulative effect associated with mixtures of organic solutes, with each solute at an activity of 0.3 or higher. A study was also conducted to determine if aqueous solutions of a good PVC swelling agent that is also totally miscible in water (acetone) can soften PVC. After 1 week a concentration of 50% acetone softened PVC while a 25% solution did not.

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Softening of Rigid PVC by
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LOUISE V. PARKER AND THOMAS A. RANNEY

INTRODUCTION

Materials used in groundwater monitoring wells must be able to withstand exposure to a variety of groundwater conditions. While it has been commonly known that certain neat organic solvents (pure product) will degrade PVC, it has not been generally known what effect high concentrations of these solvents in aqueous solutions have on the integrity of PVC well casings.

Berens (1985) and Vonk (1985, 1986) predicted the permeation of organics through PVC pipe based on samples of PVC exposed to a range of concentrations (activities) of these solvents. They noted that the solvent interaction parameter (χ) used in the Flory–Huggins equation* could be used as a measure of the solvent or swelling power of a particular solvent. Table 1 gives the χ values Berens derived for a number of organic solvents (at 30°C). Table 2 gives estimates of χ values that were determined (at 20°C) by Vonk (1985). PVC is only softened by solvents with a χ value less than 1 (Berens 1985) or 1.2 (Vonk 1985); the lower the number, the greater the solvent or swelling power. A neat solvent with a χ value less than 0.5 can completely dissolve PVC (Berens 1985) and is considered a good solvent. Compounds with χ values ranging from 0.5 to 1.0 are considered marginal solvents but strong swelling agents (Berens 1985). Thus, very few organic solvents are true "solvents" of PVC. According to Vonk (1985), PVC

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* The Flory–Huggins equation relates activity a to the volume fraction V_1 of the organic chemical in the polymer as follows:
$$\ln a = \ln V_1 + (1 - V_1) + \chi(1 - V_1)^2$$
where χ is the Flory–Huggins interaction parameter.

is nearly inert to organic solvents if their χ value is greater than 3 (e.g. alcohols, aliphatic hydrocarbons and organic acids).

Berens observed that the rate of penetration of an organic solute in PVC changed by many orders of magnitude as the activity of the penetrant in the environment changed. He noted that at ambient temperatures, rigid PVC would only be softened by strong solvents or swelling agents of PVC at activities greater than 0.5. The less aggressive the solvent (i.e. the higher the χ value), the higher the activity required to cause softening. Figure 1 shows the isotherms Berens derived using the Flory–Huggins equation for various values of χ and the approximate softening range for PVC at 30°C. Berens predicted that for lower temperatures, such as those commonly encountered in groundwater, slightly higher activities would be needed to cause softening.

For aqueous solutions the activity of a solvent can be approximated by dividing the concentration of the compound in solution by its solubility in water Thus, according to Berens, if aqueous solution of solvents are going to soften rigid PVC, the pure (or neat) solvent must be able to soften or dissolve PVC and must exist in solution at a concentration that exceeds half its solubility in water (activity >0.5).

One criticism of Berens's work is that the various solutions he used in his experiments were prepared by dissolving the organic solvents in polyethylene glycol, so he never actually tested aqueous solutions of these solvents. Since it is possible that the partitioning of these organic solutes between the dissolved state and the polymer could differ between glycol and water, studies that use aqueous solutions of PVC solvents are necessary to confirm Berens's predictions. While Vonk

Table 1. Equilibrium swelling and interaction parameters for PVC–organic liquid systems. (After Berens 1985.)

Compound	Density (g/cm^3)	Weight gain (%)	Volume fraction	Time* (hr)	Interaction parameter χ
Methylene chloride	1.34	>800**	>0.89	2	<0.53
Chloroform	1.49	227	0.68	6	0.64
Carbon tetrachloride	1.59	0	~0	(280)	—
1,1-dichloroethane	1.18	132	0.61	6	<0.68
1,2-dichloroethane	1.26	700**	>0.86	6	<0.55
1,1,1-trichloroethane	1.32	67	0.42	600	0.85
1,1,2-trichloroethane	1.44	>400**	>0.80	10	<0.56
Trichloroethylene	1.47	70	0.40	5	0.88
Tetrachloroethylene	1.63	35	0.23	800	1.17
1,2-dichloropropane	1.16	176	0.68	20	0.68
Benzene	0.88	50	0.44	12	0.83
Toluene	0.87	50–60	0.45–0.49	15	0.80
Xylene	0.87	42	0.40	100	0.88
Acetone	0.79	170	0.75	2	0.61
Methanol	0.79	~1.0	—	(300)	—
Ethanol	0.79	~0.1	—	(300)	—
i-propanol	0.79	~0.5	—	(300)	—
n-hexane	0.66	~0.6	—	(160)	—
Vinylchloride	0.89	~30	0.33		0.98

*Time to apparent equilibrium, 24-mil (0.6 mm) PVC sheet, or duration of experiment in parentheses.
**Soluble.

did use aqueous solutions of organics in his studies, we have been unable to find a thorough discussion in English of his methods.

We conducted a study that looked for softening of PVC exposed to various activities of a good PVC swelling agent (methylene chloride) in aqueous solutions (Parker et al. 1992). Small pieces of PVC well casing were exposed to solutions at activities of 0.2, 0.4, 0.6, 0.8 and 1.0 and to water only (as a control). The samples were monitored for changes in weight, length, flexibility and curvature; changes in surface structure were monitored using a scanning electron microscope. The study was conducted for 33 days. Samples exposed to the highest-activity solution (1.0) softened within the first 4 days (they became rubbery and could be bent easily by hand). Samples exposed to the 0.8-activity solution softened after 22 days (Table 3). This agrees well with Berens's predictions. Also as predicted, samples exposed to the lowest-activity solution (0.2) showed no signs of softening by the end of the study (33 days). However, samples exposed to the 0.4- and 0.6-activity solutions showed some slight changes (occasionally a sample could be bent or showed signs of curling), especially at 0.6 activity (Tables 3 and 4).

The literature is not clear whether an aqueous solution of methylene chloride with an activity of

0.6 should be able to soften PVC. Berens did not give a χ value for methylene chloride but estimated that it was less than 0.53. Vonk (1985) gave 0.55 for χ. Using Vonk's value for χ and Berens's isotherms (Fig. 1), we would predict that softening should not occur at this activity. However, if the true χ value of methylene chloride were 0.3 (or less), then softening should occur (at 30°C). Berens also predicted that softening would not occur in solutions with an activity of 0.4, even if the solvent had a χ value of 0.0. Thus, if softening did (or does) occur in either the 0.4- or 0.6-activity solution, it is possible that methylene chloride favors partitioning into PVC from an aqueous solution more than from the glycol solution used by Berens (1985). This would mean that for aqueous solutions, softening occurs at slightly lower activities than Berens predicted. However, the problem with our previous study (Parker et al. 1992) was that the method used to determine softening (i.e. bending the sample) was subjective and lacked quantification.

This report describes several studies (of both methylene chloride and TCE) that address the softening of PVC by aqueous solutions of PVC swelling agents at intermediate and lower activities. In addition, this report also describes two studies that address two other topics not addressed by either Berens or Vonk: the softening of PVC by

Table 2. Estimates of the Flory–Huggins interaction parameter χ*. (After Vonk 1985.)

Organic compound	χ
Benzene	0.83
Toluene	0.82
o-xylene	0.76
m-xylene	0.87
p-xylene	0.86
Ethylbenzene	0.89
1,3,5-trimethylbenzene	2.52
Propylbenzene	1.91
Methylethylketone	0.54
Di-isopropylketone	0.56
Methylene chloride	0.55
1,2-dichloroethane	0.56
1,1,1-trichloroethane	0.92
1,1,2-trichloroethane	0.58
1,1,2,2-tetrachloroethane	0.59
1,2-dichloropropane	0.65
Perchloroethylene	1.58
Trichloroethylene	0.90
Chlorobenzene	0.66
1,2-dichlorobenzene	0.63
1,3-dichlorobenzene	0.74
1,2,4-trichlorobenzene	1.52
o-chlorotoluene	0.74
m-chlorotoluene	0.69
p-chlorotoluene	0.75
Nitrobenzene	0.54
Aniline	0.87
2-chloroaniline	0.58
3-chloroaniline	0.61
n-methylaniline	0.59

*For segments of PVC pipe (O.D. = 32 mm and wall thickness = 1.6 mm) immersed in pure liquid compounds for 410 days at 20 ± 3°C.
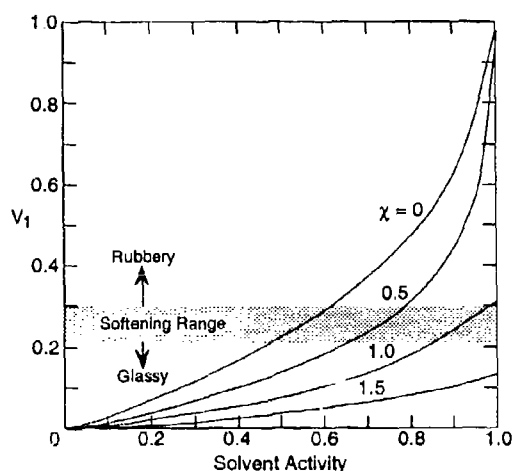
Figure 1. Flory–Huggins isotherms for various values of χ and approximate composition for softening of PVC at room temperature. (After Berens 1985.)

Table 3. Observed changes in flexibility* of PVC samples exposed to aqueous solutions of methylene chloride. (From Parker et al. 1992.)

Time (days)	Activity = 0.2	0.4	0.6	0.8	1.0
4	0	0	0	1	2
8	0	0	0	1	2
15	0	0	1	2	2
22	0	0	1	2	2
33	0	1	1	2	2

*Rankings: 0—no noticeable flexibility; 1—more flexibility than original; 2—can be bent back over itself.

aqueous solutions containing 1) a mixture of several organic solutes and 2) a PVC swelling agent that is totally miscible in water. These are referred to as the mixed-organic-solute study and the acetone study, respectively. To obtain more quantitative data than that we obtained in the previous study, we used a Barcol impressor to measure the hardness of the PVC pieces (ASTM 1988).

Methylene chloride studies

As a follow-up to our previous study (Parker et al. 1992), these studies looked for softening of PVC by aqueous solutions of methylene chloride at intermediate activities (0.4–0.8) and lower activities (0.05–0.4).

Trichloroethylene studies

We selected a second swelling agent of PVC: trichloroethylene (TCE), which has a χ value rang-

Table 4. Observed changes in curvature* of PVC samples exposed to aqueous solutions of methylene chloride. (From Parker et al. 1992.)

Time (days)	Activity = 0.2	0.4	0.6	0.8	1.0
4	0	0	0	1	2
8	0	0	1	1	2
15	0	0	1	1	2
22	0	0	1	2	2
33	0	1	1	2	2

*Rankings: 0—no noticeable flexibility; 1—some curvature or twisting in at least one of the three samples; 2—obvious curvature or twisting in at least two of the three samples.

ing from 0.88 (Berens 1985) to 0.90 (Vonk 1985). TCE is one of the most common organic pollutants in the environment.

Mixed-organic-solutes study

Neither Berens nor Vonk addressed what effect an aqueous solution that contained a mixture of several organic solutes would have on PVC. Since one is much more likely to encounter groundwater that contains a mixture of organic contaminants, this is an important question for the groundwater monitoring industry.

This study looked for the softening of PVC by an aqueous solution that contained three good swelling agents of PVC; all three of these organic compounds have χ values less than 0.6. The activity of each organic solute was 0.3. Using Berens's isotherms (Fig. 1), we predicted that any solvent with a χ value less than 0.6 and an activity of 0.3 would not soften PVC. However, if these organic solutes have a cumulative or interactive effect, then this solution could soften PVC.

Acetone study

Another issue that has not been addressed in the literature is whether a good PVC swelling agent or solvent that is also miscible in water can soften PVC when mixed with water. As mentioned previously, activity can be approximated by dividing the concentration of an organic compound in solution by its solubility in water. Clearly this cannot be done for a substance that is miscible in water, since this would mean dividing by an infinite number.

This study looked to see if acetone, which is a good swelling agent of PVC [χ =0.61 (Berens 1985)] and is totally miscible in water, can soften PVC when dissolved in water. In this study, pieces of PVC were subjected to several concentrations of acetone, ranging from 0.05% to 75%.

MATERIALS AND METHODS

Small pieces of PVC were cut from 5.1-cm- (2-in.-) diameter schedule-40 well casing. The overall dimensions of the pieces were approximately $9 \times 9 \times 0.8$ mm (l × w × h), giving a total surface area of approximately 1.9 cm^2 and an approximate weight of 0.09 g. Special care was taken to eliminate contamination from grease or oil during the cutting procedure. Throughout the study, all the samples were handled using stainless steel forceps.

The test solutions were made up in 22-mL boro-

silicate glass vials with aluminum-lined, Teflon-backed plastic caps. The vials were filled almost to the top with Milli-Q water, and a volume of solvent appropriate for each activity was added using a microliter syringe. The vials were then filled to capacity with water to eliminate any headspace, capped and placed on an orbital shaking table for approximately 100 hours to assure mixing of the solvent–water phases. Vials were checked using a magnifying glass to determine that no small droplets of solvent remained undissolved. After mixing, the vials were opened and previously weighed pieces of PVC were added to the solutions. A few drops of water were added to ensure that there was no headspace, and the vials were recapped. The samples were kept in the dark at room temperature.

On the sampling day the pieces of PVC were removed from the solution, placed on paper towels, blotted and allowed to air dry for 1 minute before weighing. Immediately after weighing, a Model 935 Barcol impressor was used to measure the hardness of the PVC. A description of the use of the Barcol impressor on rigid plastics can be found in ASTM Standard Test Method D2583-87 (ASTM 1988). However, the impressor employed in this study is made for indenting softer plastics and is not the model described in the ASTM test method. This model was selected so that measurements could be taken during the softening process.

Methylene chloride studies

First short-term study

The activities of the test solutions in this study were 0.4, 0.6, 0.8 and 0.0 (controls, which were samples with only water and PVC). Activities were based on a solubility of 19,000 mg/L of methylene chloride in water. This value was selected from among those given by Montgommery and Welkom (1990) because it agreed with the value our laboratory experimentally determined.[*] The pieces of PVC were exposed to the test solutions for 4, 8, 24, 48, 72 and 168 hours (7 days). There were three replicates for each treatment and time.

Second short-term study

This study was identical to the previous study except that there were five replicates per treatment

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and time, and the solutions were gently shaken on a platform shaker to enhance contact between the test solutions and the surfaces of the PVC pieces.

Long-term study

The activities of the test solutions in this study were 0.4, 0.2, 0.1, 0.05 and 0.0 (controls). The sample times were 1, 2, 3, 4, 6, 8, 12, 16 and 20 weeks. There were three replicates for each activity and sample time.

Trichloroethylene studies
First study

The activities of the test solutions in this study were 1.0, 0.8, 0.6, 0.4, 0.2 and 0.0 (controls). Activities were based on a maximum solubility of 1000 mg/L (as found in Dean 1985). The contact times were 4, 8, 15, 22, 33 and 68 days. Each week the remaining pieces of PVC were placed into freshly prepared TCE solutions and returned to storage. Thus, no piece of PVC stayed in any solution longer than 7 days. This was done to maintain the solvent stress on the PVC and thereby promote maximum sorption. There were three replicates for each treatment and time.

Second study

To confirm findings from the first study, we performed a similar study. The methods used in this study were similar to those used in the first study, with the following exceptions:
- There was only one set of samples taken;
- The contact time was longer: 11 weeks (77 days);
- There were 10 replicates for each treatment; and
- The samples were shaken gently on a platform shaker to improve contact between the test solutions and the surfaces of the PVC pieces.

Mixed-organic-solute study

Three good PVC swelling agents were used in this study: methylene chloride (χ < 0.53 from Berens 1985; χ = 0.55 from Vonk 1985); 1,1,2-trichloroethane (χ < 0.56 from Berens 1985; χ = 0.58 from Vonk 1985); and 1,2-dichloroethane (χ < 0.55 from Berens 1985; χ = 0.56 from Vonk 1985). The activity of each organic solute was 0.3. These activities were based on the following solubilities: 19,000 mg/L for methylene chloride; 4,400 mg/L for 1,1,2-trichloroethane (McNally and Grob 1984); and 8,500 mg/L for 1,2-dichloroethane (McConnell et al. 1975, as given by Montgomery and Welkom 1990). Sample times were 2, 4, 7, 14 and 21 days. There were three replicates for each treatment and time.

Acetone study

The purpose of this screening test was to determine if a miscible swelling agent of PVC (acetone) could soften PVC when diluted in water. Since this was a screening test, there was only one replicate for each concentration and time in this study. The concentrations were 0.05, 0.5, 5, 25, 50 and 75% (wt/vol, g/mL), and the sample times were 3 and 7 days.

RESULTS AND DISCUSSION

Methylene chloride studies
First short-term study

This study looked for softening at three intermediate activities (0.4, 0.6 and 0.8) during a one-week period. Table 5 gives the Barcol readings for the different activities and times. Appendix Table A1 gives the percent weight gain for the samples with time. Analysis of Variance tests and Duncan's New Multiple Range tests were conducted on the Barcol readings for each time and treatment to determine which treatments were significantly different from the controls. By the end of this study the Barcol readings of samples exposed to the 0.8 and 0.6 activities were significantly lower than those of the controls (Table 5), indicating that softening had occurred. The Barcol readings for samples exposed to the 0.4-activity solutions were slightly lower (~5% for the means), but this difference was not significant (Table 5). The final weight gains for samples exposed to the 0.6- and 0.8-activity solutions were more than 10%, while the weight gains were less than 1% for the samples exposed to the 0.4-activity solutions. The changes in hardness readings agree with what we observed when we tried to bend these samples. The samples exposed to the 0.6- and 0.8-activity solutions could be bent easily; the samples exposed to the 0.4-activity solutions could not. This indicates that the samples exposed to the 0.6- and 0.8-activity solutions had become plasticized or rubbery.

Second short-term study

Because some of the data were inconsistent and highly variable for the samples exposed to the 0.8- and 0.6-activity solutions in the previous study, we decided to repeat this experiment. This time, we used a larger sample size (five replicates per treatment), and we gently shook these samples to enhance interaction between the solutions and the surfaces of the PVC. Table 6 gives the Barcol readings for this study, and Appendix Table A2 gives

Table 5. Hardness (Barcol) values of PVC for various contact times in the first short-term methylene chloride study.

Activity	4	8	24	48	72	168 hours
0.0 control	76	79	78	74	78	75
0.0 control	79	76	78	76	78	76
0.0 control	76	72	76	72	75	77
$\bar{X}$	77[a]	75.7[a]	77.3[a]	74[a]	77[a]	76[a]
S.D.	1.7	3.5	1.2	2	1.7	1
RSD(%)	2.2	4.6	1.5	2.7	2.2	1.3
0.4	77	76	73	75	76	76
0.4	76	76	76	76	76	69
0.4	76	76	76	74	71	72
$\bar{X}$	76.3[a]	76[a]	75[a]	75[a]	74.3[a]	72.3[a]
S.D.	0.6	0	1.7	1	2.9	3.5
RSD(%)	0.8	0	2.3	1.3	3.9	4.9
0.6	72	71	73	70	70	40
0.6	75	74	67	65	62	41
0.6	74	76	73	73	58	57
$\bar{X}$	73.7[a]	73.7[a]	71[a]	69.3[a]	63.3[a]	46[b]
S.D.	1.5	2.5	3.5	4	6.1	9.5
RSD(%)	2.1	3.4	4.9	5.8	9.6	20.7
0.8	68	73	57	21	23	5
0.8	61	56	52	56	62	21
0.8	58	61	17	16	46	13
$\bar{X}$	62.3[b]	63.3[b]	42[b]	31[b]	43.7[b]	13[c]
S.D.	5.1	8.7	21.8	21.8	19.6	8
RSD(%)	8.2	13.8	51.9	70.3	44.9	61.5

$\bar{X}$ = mean
S.D. = standard deviation
RSD(%) = percent relative standard deviation
For each time, treatments with the same letter were not significantly different.

the percent weight gain data. These results agreed well with our findings in the previous study. Analysis of Variance and Duncan's New Multiple Range tests indicated that by the end of the study (7 days), the Barcol readings of the samples exposed to the 0.6 and 0.8 solutions were significantly lower than the Barcol readings of the controls (Table 6). While the Barcol readings for the samples exposed to the 0.4-activity solutions for 72 hours were significantly lower than the controls (the mean loss was 2.4%), after 7 days there was no significant difference (even though the mean loss was slightly more [3.2%]) (Table 6). Again, the change in the hardness readings agreed reasonably well with what we observed when we tried to bend the samples. The samples exposed to the 0.6- and 0.8-activity solutions appeared rubbery (they could be easily bent), while those exposed to the 0.4-activity solution did not. By the end of the study the weight gain for samples exposed to the 0.6- and 0.8-activ-

ity solutions exceeded 9%, while the weight gain for samples exposed to the 0.4-activity solutions was less than 1.5%.

Long-term study

The question that the last study did not answer is: with time, do pieces of PVC exposed to 0.4-activity solutions of methylene chloride also soften? This study attempted to answer that question and also looked for softening at even lower activities. Pieces of PVC were exposed to 0.4-, 0.2-, 0.1- and 0.05-activity solutions for 20 weeks. Analysis of Variance tests and Duncan's New Multiple Range tests revealed that by the end of the study, the Barcol readings for samples exposed to the 0.4-, 0.2- and 0.1-activity solutions were significantly lower than those of the control samples (Table 7). There was no significant difference between the hardness readings of the samples exposed to the 0.05 solutions and the controls. While the Barcol

Table 6. Hardness (Barcol) values of PVC for various contact times in the second short-term methylene chloride study.

Activity	4	8	24	48	72	168 hours
0.0 control	74	76	76	74	76	75
0.0 control	76	73	77	76	73	73
0.0 control	73	76	74	74	74	75
0.0 control	74	73	74	77	75	76
0.0 control	73	75	76	74	75	75
$\bar{X}$	74[a]	74.6[a]	75.4[a]	75[a]	74.6[a]	74.8[a]
S.D.	1.2	1.5	1.3	1.4	1.1	1.1
RSD(%)	1.5	1.8	1.6	1.7	1.4	1.3
0.4	74	73	77	77	72	74
0.4	73	76	74	76	73	71
0.4	74	74	74	75	73	72
0.4	75	75	75	74	74	70
0.4	74	74	75	74	72	75
$\bar{X}$	74[a]	74.4[a]	75[a]	75.2[a]	72.8[b]	72.4[a]
S.D.	0.7	1.1	1.2	1.3	0.8	2.1
RSD(%)	0.9	1.4	1.5	1.6	1	2.6
0.6	73	75	63	66	66	56
0.6	73	74	72	62	65	59
0.6	74	73	68	67	63	58
0.6	72	75	66	67	6(	56
0.6	73	72	67	65	64	60
$\bar{X}$	73[a]	73.8[a]	67.2[b]	65.4[b]	64.8[c]	57.8[b]
S.D.	0.7	1.3	3.3	2.1	1.3	1.8
RSD(%)	0.9	1.6	4.4	2.8	1.8	2.8
0.8	57	38	29	25	25	32
0.8	58	37	24	24	23	28
0.8	55	42	24	23	24	33
0.8	56	39	28	28	26	30
0.8	54	37	30	24	27	28
$\bar{X}$	56[b]	38.6[b]	27[b]	24.8[b]	25[d]	30.2[c]
S.D.	1.6	2.1	2.8	1.9	1.6	2.3
RSD(%)	2.5	4.8	9.4	6.9	5.7	6.8

For each time, treatments with the same letter were not significantly different.

readings for samples exposed to the 0.2- and 0.4-activity solutions became significantly lower than the controls earlier in the study, it was not until the end of the study that the hardness readings for samples exposed to the 0.1-activity solutions became significantly different from the controls.

By the end of the study the changes in the hardness readings for all the samples were all small (<10%), and the weight gain never exceeded 4.5% (Appendix Table A3). This may explain why none of the samples appeared rubbery (we were not able to bend any of these samples by hand).

We conclude from these studies that methylene chloride, a good PVC swelling agent, is able to cause a small but statistically significant change in the hardness readings of PVC samples exposed to activities as low as 0.1 at 20°C. We believe this indicates that softening has begun. During the time frame of these studies, PVC became rubbery at activities as low as 0.6. Thus, softening occurred at much lower activities than Berens predicted or Vonk reported for other similar PVC solvents. While there is no evidence that softening would eventually occur in a 0.05-activity solution of methylene chloride, this is a possibility. A longer-term study would answer this question.

Trichloroethylene studies
First study

In this study, pieces of PVC were exposed to solutions of various activities (1.0, 0.8, 0.6, 0 4 and 0.2) for up to 68 days. Table 8 gives the Barcol

Table 7. Hardness (Barcol) values of PVC for various contact times in the long-term methylene chloride study.

Activity	1	2	3	4	6	8	12	16	20 weeks
0.00 control	75	74	73	72	74	72	76	73	77
0.00 control	72	75	75	76	76	76	75	74	76
0.00 control	76	76	75	75	76	73	74	75	77
X̄	74.3[a]	75[a]	74.3[a]	74.3[a]	75.3[a]	73.7[a]	75[a]	74[a]	76.7[a]
S.D.	2.1	1.0	1.2	2.1	1.2	2.1	1.0	1.0	0.6
RSD(%)	2.8	1.3	1.6	2.8	1.5	2.8	1.3	1.4	0.8
0.05	75	76	71	76	75	76	74	75	76
0.05	74	74	72	75	75	75	73	74	76
0.05	74	73	73	73	74	76	76	76	76
X̄	74.3[a]	74.3[a]	72[a,b]	74.7[a]	74.7[a]	75.7[a]	74.3[a]	75[a]	76[a]
S.D.	0.6	1.5	1.0	1.5	0.6	0.6	1.5	1.0	0.0
RSD(%)	0.8	2.1	1.4	2	0.8	0.8	2.1	1.3	0
0.10	73	70	76	68	73	70	75	76	72
0.10	72	75	73	72	75	73	74	74	71
0.10	73	76	73	73	74	75	72	72	69
X̄	72.7[a]	73.7[a]	74[a]	71[b]	74[a]	72.7[a,b]	73.7[a]	74[a,b]	70.7[b,c]
S.D.	0.6	3.2	1.7	2.6	1.0	2.5	1.5	2.0	1.5
RSD(%)	0.8	4.4	2.3	3.7	1.4	3.5	2.1	2.7	2.2
0.20	75	75	72	74	73	75	70	68	73
0.20	72	76	68	75	76	76	73	74	72
0.20	74	76	72	76	75	74	74	72	72
X̄	73.7[a]	75.7[a]	70.7[b]	75[a]	74.7[a]	75[a]	72.3[a,b]	71.3[b]	72.3[b]
S.D.	1.5	0.6	2.3	1.0	1.5	1.0	2.1	3.1	0.6
RSD(%)	2.1	0.8	3.3	1.3	2	1.3	2.9	4.3	0.8
0.40	74	72	71	74	73	70	65	71	67
0.40	74	74	73	73	76	74	71	72	69
0.40	73	74	72	73	72	70	70	70	71
X̄	73.7[a]	73.3[a]	72[a,b]	73.3[a,b]	73.7[a]	71.3[b]	68.7[b]	71[b]	69[c]
S.D.	0.6	1.2	1.0	0.6	2.1	2.3	3.2	1.0	2.0
RSD(%)	0.8	1.6	1.4	0.8	2.8	3.2	4.7	1.4	2.9

For each time, treatments with the same letter were not significantly different.

readings and Appendix Table A4 shows the weight gains. Analysis of Variance tests and Duncan's New Multiple Range tests of the Barcol readings revealed that by the end of the experiment, samples exposed to the 0.6-, 0.8- and 1.0-activity solutions had Barcol readings that were significantly lower than for the controls (Table 8). However, none of these samples appeared to be plasticized or rubbery, as they could not be bent. The weight gains for these samples were all less than 5%, except for the samples exposed to the 1.0-activity solutions (where the mean weight gain was 11.6%).

Using Berens's isotherms, we would predict that (at 30°C) an organic solvent with a χ value similar to that of TCE (0.88 from Berens 1985, 0.90 from Vonk 1985) would soften PVC at activities of 0.8 and greater, and PVC would appear rubbery at an activity of approximately 0.95. Thus, for this solvent also, softening occurred at lower activities than Berens would predict.

Second study

To confirm our findings, we repeated the last set of samples taken in the previous study. To improve our ability to observe a significant change by the end of the study, we made the following changes:
- There were 10 replicates for each treatment;
- The samples were slowly shaken on a platform shaker to improve contact between the solutions and the various sides of the test pieces; and
- The contact time was slightly longer (77 vs. 68 days).

Table 9 and Appendix Table A5 give the results from this study. Although the total weight gain was higher for all the treatments except the con-

Table 8. Hardness (Barcol) values of PVC for various contact times in the first TCE study.

Activity	4	8	15	22	33	68 days
0.0 control	73	72	75	74	73	75
0.0 control	75	73	74	75	75	73
0.0 control	74	73	74	73	72	75
$\bar{X}$	74.0[a]	72.7[a]	74.3[a]	74.0[a]	73.3[a]	74.3[a]
S.D.	1.0	0.6	0.6	1.0	1.5	1.2
RSD (%)	1.4	0.8	0.8	1.4	2.1	1.6
0.2	74	74	74	74	74	73
0.2	73	73	77	74	75	75
0.2	75	73	74	75	74	74
$\bar{X}$	74.0[a]	73.3[a]	73.3[a]	74.3[a]	74.3[a]	74.0[a,b]
S.D.	1.0	0.6	1.2	0.6	0.6	1.0
RSD (%)	1.4	0.8	1.6	0.8	0.8	1.4
0.4	75	74	74	73	75	73
0.4	74	74	73	75	72	75
0.4	75	72	73	73	74	73
$\bar{X}$	74.7[a]	73.3[a]	73.3[a]	73.7[a]	73.7[a]	73.7[a,b]
S.D.	0.6	1.2	0.6	1.2	1.5	1.2
RSD (%)	0.8	1.6	0.8	1.6	2.1	1.6
0.6	73	73	74	75	73	70
0.6	75	73	75	75	71	71
0.6	74	73	74	76	75	73
$\bar{X}$	74.0[a]	73.0[a]	74.3[a]	75.3[a]	73.0[a]	71.3[b,c]
S.D.	1.0	0.0	0.6	0.6	2.0	1.5
RSD (%)	1.4	0	0.8	0.8	2.7	2.1
0.8	75	74	71	72	74	71
0.8	74	72	74	74	73	69
0.8	72	72	73	75	75	71
$\bar{X}$	73.7[a]	72.7[a]	72.7[a]	73.7[a]	74.0[a]	70.3[c]
S.D.	1.5	1.2	1.5	1.5	1.0	1.2
RSD (%)	2.1	1.6	2.1	2.1	1.4	1.6
1.0	73	74	73	71	69	57
1.0	73	72	74	71	65	61
1.0	74	74	73	72	65	57
$\bar{X}$	73.3[a]	73.3[a]	73.3[a]	71.3[b]	66.3[b]	58.3[d]
S.D.	0.6	1.2	0.6	0.6	2.3	2.3
RSD (%)	0.8	1.6	0.8	0.8	3.5	4

For each time, treatments with the same letter were not significantly different.

trols, we did not find a statistically significant difference in the hardness readings of those samples exposed to the 0.6-activity solutions when compared with the control samples (Table 9). Only the samples exposed to the 0.8- and 1.0-activity solutions had hardness readings that were significantly lower than the controls, and the samples exposed to the 1.0-activity solutions were flexible enough to be bent easily. These results agree with what you would predict using Berens's isotherms (Fig. 1) (for systems at 30°C). The weight gains were less than 5% except for those samples ex-

posed to solutions with an activity of 1.0 (where the mean weight gain was 18.6%).

When we compared these results with those from the previous study, we concluded that there is no consistent trend for the samples exposed to the 0.6-activity solutions. This may be because the change we observed is real but very small and that given more time, softening would be more pronounced, or it may be that the PVC is very heterogeneous, giving different results for different pieces. Using Berens's isotherms, we would predict that at 20°C softening of PVC should occur at

Table 9. Hardness (Barcol) values of PVC for various activities in the second TCE study.

78	76	76	77	73	40
76	78	74	74	72	78
75	77	78	78	73	80
77	74	77	77	76	44
78	77	76	74	71	42
76	78	77	77	73	44
74	77	78	74	73	41
76	75	77	76	74	44
77	76	78	77	76	42
78	76	75	76	71	41
$\bar{X}$ 76.4^a	76.4^a	76.3^a	75.9^a	73.4^b	38.5
S.D. 1.4	1.3	1.3	1.5	1.8	3.3
RSD (%) 1.9	1.7	1.8	2.0	2.5	8.7

Treatments with the same letter were not significantly different. Measurements were made after 11 weeks of contact time.

activities that are *greater* than 0.8. The fact that we found softening *at* activities of 0.8, and possibly at 0.6, indicates that softening of PVC in aqueous solutions may occur at slightly lower activities than Berens predicted. This issue could be resolved by a long-term study as was conducted for methylene chloride.

Mixed-organic-solute study

In this study, pieces of PVC were exposed to an aqueous solution that contained three good PVC swelling agents (methylene chloride; 1,1,2-

trichloroethane and 1,2-dichloroethane; $\chi = 0.6$ for each compound) each at an activity of 0.3. At this activity level, none of these organic solutes should be able to soften PVC by themselves, at least in the time frame of this study. [In fact, previous studies showed no significant change in the hardness readings for samples exposed to a solution containing one of these swelling agents (methylene chloride) at a slightly higher activity (0.4) until 8 weeks had passed.] Analysis of Variance and Duncan's New Multiple Range tests of these data revealed that after two days, the Barcol readings of the samples exposed to the organic solutions were significantly lower than those of the controls (Table 10). These samples were rubbery and could be bent easily. By the end of the study (21 days), the total weight gain was around 10% for these samples (Appendix Table A6). This weight gain was less than what we observed for samples exposed to a 0.9-activity solution of methylene chloride (25% in 7 days) but much greater than what we observed for samples exposed to a 0.4-activity solution for 21 days (1.5%). Thus, there is evidence of a cumulative or interactive effect for solutions containing multiple organic solutes that are PVC solvents or good swelling agents, when the activity of each organic solute is 0.3 or more.

Acetone study

Since there was only one sample for each concentration and time in this study, no statistical analyses could be conducted on these data. However, we did see a very large change in the Barcol

Table 10. Hardness (Barcol) values of PVC for various contact times in the mixed-organic-solute study.

Treatment	2	4	7	14	21 days
control	76	72	73	72	74
control	77	74	75	73	74
control	75	73	74	75	77
$\bar{X}$	76.0^a	73.0^a	74.0^a	73.3^a	75.0^a
S.D.	1.0	1.0	1.0	1.5	1.7
RSD (%)	1.3	1.4	1.4	2.1	2.3
organic solution	54	55	68	37	52
organic solution	57	62	56	46	64
organic solution	60	54	48	58	62
$\bar{X}$	57.0^b	57.0^b	57.3^b	47.0^b	59.3^b
S.D.	3.0	4.4	10.1	10.5	6.4
RSD (%)	5.3	7.6	17.6	22.4	10.8

For each time, treatments with the same letter were not significantly different.

Solution concentration (%)	3	7 days
control	77	76
0.05	77	75
0.5	74	75
5	76	77
25	73	72
50	65	64
75	23	26

readings after 3 days for the samples exposed to the 50% and 75% solutions (Table 11). These samples were rubbery and could be bent easily by hand. In contrast, by the end of the study (7 days) the Barcol readings for the samples exposed to the 5, 0.5 and 0.05% solutions did not appear to be different from those of the control samples. There may have been some change in the samples exposed to the 25% solution, as the Barcol readings were slightly lower. The weight gain after 7 days was less than 1% for all the samples except those exposed to the 50 and 75% solutions (the weight gains were 4.8 and 18.7%, respectively) (Appendix Table A7).

We conclude that for acetone, a 50% solution rapidly softens PVC. A long-term study would better define the effects of lower concentrations of acetone on PVC.

SOFTENING AND DIFFUSION IN PVC

We were able to see statistically significant changes in the Barcol readings long before the samples became pliable or rubbery. For samples exposed to solutions of methylene chloride, PVC became pliable when the Barcol readings ranged from 57 to 66, and it became rubbery when the Barcol readings were less than 57. Generally the control values ranged from 73 to 76. We do not know whether the samples exposed to the 0.4-, 0.2- and 0.1-activity solutions of methylene chloride would eventually become rubbery, as those at the higher activities did. Since the long-term study did not go long enough to reach equilibrium at these activities, a longer-term study is needed. It may be that the polymer becomes only partially softened. Generally PVC became rubbery when the weight gain exceeded 6%. Our results with TCE are less

definitive. It appears that, as Berens predicted, TCE does not soften PVC at as low an activity as methylene chloride can. A longer-term study is needed to better define the softening range and to determine if softening also occurs at lower activities than Berens predicted for this solvent.

At the lowest activities, diffusion of organic solutes in rigid PVC will be purely Fickian and thus concentration-independent and slowest (Berens 1985, Vonk 1985, 1986, Jenkins et al. 1986, Holsen 1988). At these activities the rate of diffusion is considered to be so slow that diffusion of an organic solute through PVC pipe would take thousands of years (Berens 1985, Vonk 1985, 1986, Olson et al. 1987). At higher activities, diffusion becomes successively concentration-dependent, then anomalous and finally Case II, and the rate of diffusion increases by several orders of magnitude (Berens 1985, Vonk 1985, 1986, Jenkins et al. 1986, Holsen 1988). With Case II, or frontal, diffusion there is a distinct transition from the glassy to the softened state. The greater the ability of the organic to swell the polymer, the lower the activity required to move from purely Fickian to other diffusion mechanisms.

There is some disagreement regarding the activity level where diffusion in PVC pipe becomes greater than Fickian. Berens predicted that Fickian diffusion occurs only if the activity of the solution is less than 0.25. However, Vonk (1985, 1986) felt that while diffusion would be Fickian for poorer PVC swelling agents (e.g. alkylated aromatics) at activities less than 0.25, the activity should be less than 0.1 for solvents and better swelling agents (e.g. anilines, chlorinated hydrocarbons, ketones and nitrobenzenes).

According to Berens, for the kinetics of diffusion to be Fickian, a plot of percent weight gain vs. square root of time should be linear for the first half of the sorption process and then should asymptotically approach the equilibrium uptake. For example, in Figure 2, Berens described the kinetics for sorption of TCE by PVC as Fickian for the 0.6-activity solution and non-Fickian for the 0.8- and 0.7-activity solutions. When our weight gain data are plotted in a similar fashion (Fig. 3), it becomes evident that, even though statistical analyses indicated that softening was occurring in some of the samples exposed to solutions at intermediate activities, diffusion was still Fickian. This was true for samples exposed to the 0.4-, 0.2- and 0.1-activity solutions in the long-term methylene chloride study and for the 0.6- and 0.8-activity solu-
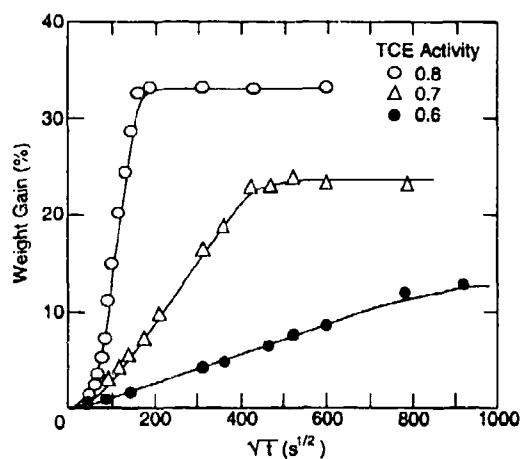
11

Figure 2. Weight gain vs. the square root of time for liquid immersion of a 0.3-mm PVC sheet in trichloroethylene–polyethylene glycol mixtures at three activities. (After Berens 1985.)
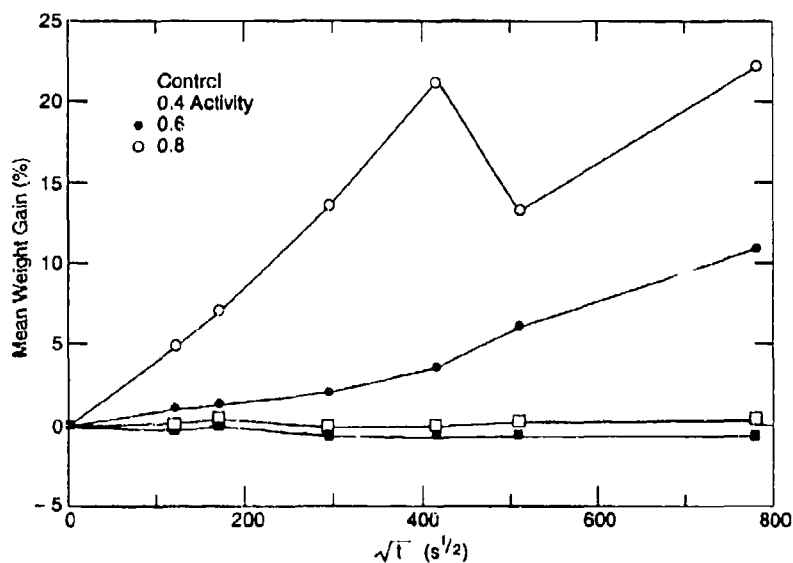
a. First short-term MC study.
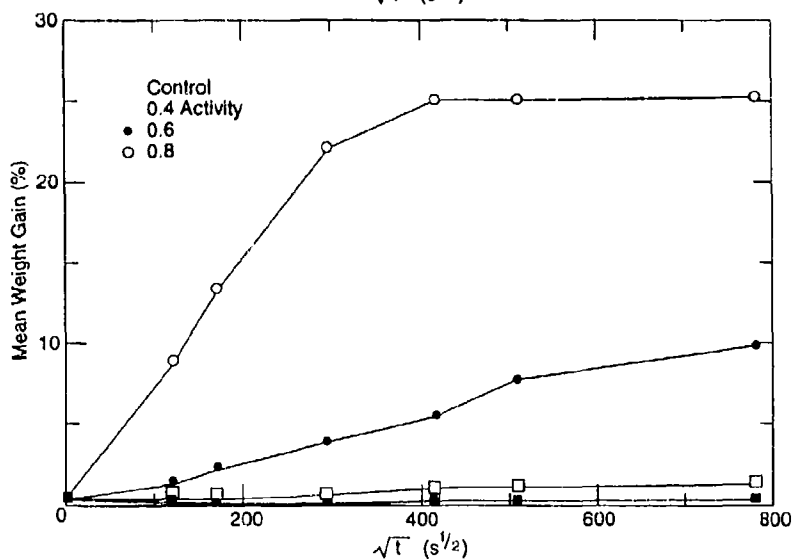
b. Second short-term MC study.

Figure 3. Weight gain vs. the square root of time for four of the studies.

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tions in the first TCE study. In Figure 3b it is not clear whether diffusion in the samples exposed to the 0.6-activity solutions was Fickian or non-Fickian; more points are needed to make this determination. (These samples were rubbery and could be bent easily.) Diffusion was clearly non-Fickian at higher concentrations (for samples exposed to 0.8-activity solutions of methylene chloride and 1.0-activity solutions of TCE). Further study would clarify whether diffusion remains Fickian for those samples exposed to the lower-activity solutions that also showed significant changes in the Barcol readings but were not yet rubbery.

CONCLUSIONS AND RECOMMENDATIONS

For the best PVC swelling agents ($\chi = 0.5$), such as methylene chloride, there is statistical evidence that PVC is softened by exposure to aqueous solutions with activities as low as 0.1 (at 20°C), which is much lower than Berens predicted or Vonk reported. The transformation of
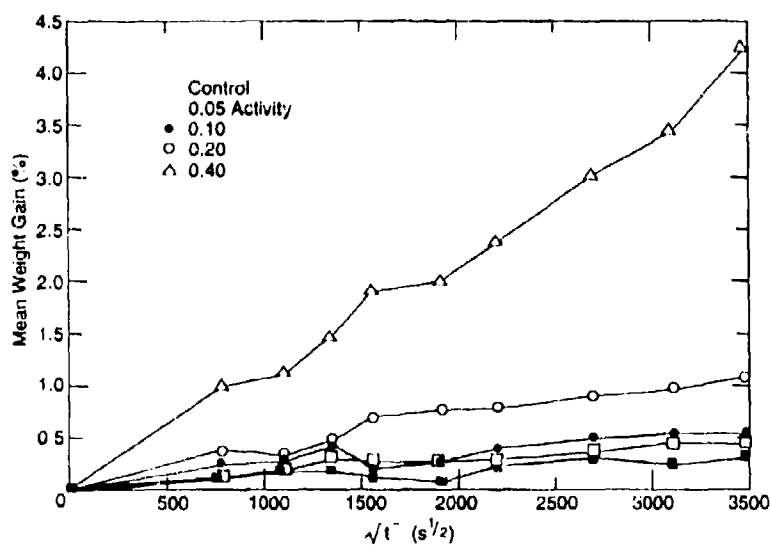
c. Long-term MC study.
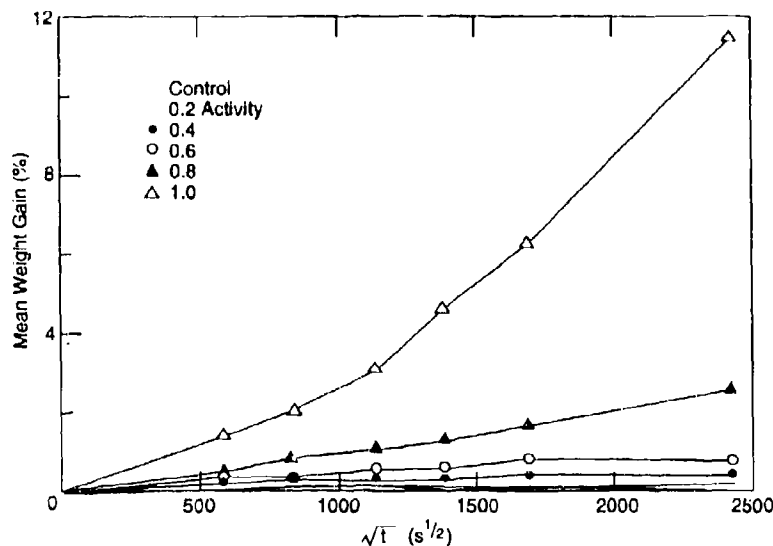
d. First TCE study.

Figure 3 (cont'd).

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rigid PVC to a rubbery state also appears to occur at a lower activity than Berens predicted. It is not clear whether softening would occur at even lower activities (<0.1) if given more time, but this cannot be ruled out. For organic solvents that are not as good swelling agents of PVC, such as TCE (with $\chi = 0.9$), softening does not appear to occur at activities much below 0.6. However, our studies with TCE were relatively short term, and we never reached equilibrium at the lower activities. Thus, we do not know if softening occurs at lower activities than Berens predicted for this solvent. Future studies will have to be even more long range.

While these studies indicate that softening occurs at lower activities than initially predicted for good swelling agents, we would also anticipate that temperature may partially counteract this trend in a monitoring well. Softening should occur at slightly higher activities at the lower temperatures typical in groundwater, although this aspect has not been researched.

The mixed-organic-solute study clearly showed that when dealing with an aqueous mixture of organic solutes that are good swelling agents of PVC, there is some type of cumulative or interactive effect among the solutes, and softening can result when the activities of each solute are 0.3. Future studies should look at mixtures containing more solutes that are at lower activities.

The acetone study showed that high concentrations of a good PVC swelling agent that is also miscible in water can cause rapid softening. Further research should look at the long-term effects of lower concentrations.

It is unfortunate that more definitive guidance on the use of PVC in the presence of low-activity PVC swelling agents cannot be given at this time.

LITERATURE CITED

ASTM (1988) Standard test method for indentation hardness of rigid plastics by means of a Barcol impressor. Method D2583-87, American Society for Testing and Materials, Philadelphia, Pa., p. 337–339.

Berens, A.R. (1985) Prediction of organic chemical permeation through PVC pipe. *Journal of the American Water Works Association*, p. 57–65.

Dean, J.I. (Ed.) (1985) *Lange's Handbook of Chemistry*. Thirteenth Edition. New York: McGraw-Hill Publishers.

Holsen, T.M. (1988) The effect of soils on the permeation of plastic pipes by organic chemicals. Ph.D. Thesis, University of California–Berkeley. University Microfilms International Dissertation Information Service, order number 8902122.

Jenkins, D., R.E. Selleck, L. Bontoux and D. Soong (1986) Permeation of plastic pipes: Literature review and research needs. SEEHRL Report 86-12, Sanitary Engineering and Environmental Health Research Laboratory, College of Engineering, School of Public Health, University of California–Berkeley.

McConnell, G., D.M. Ferguson and C.R. Pearson (1975) Chlorinated hydrocarbons and the environment. *Endeavor*, 34(121): 13–18.

McNally, M.E. and R.L. Grob (1984) Headspace determination of solubility limits of the base neutral and volatile components from the Environmental Protection Agency's list of priority pollutants. *Journal of Chromatography*, 284: 105–116.

Montgommery, J.H. and L.M. Welkom (1990) *Groundwater Chemicals Desk Reference*. Chelsea, Michigan: Lewis Publishers, Inc.

Olson, A.J., D. Goodman and J.P. Pfau (1987) Evaluation of permeation of organic solvents through PVC, asbestos/cement, and ductile iron pipes. *Journal of Vinyl Technology*, 9(3): 114–118.

Parker, L.V., T.A. Ranney and S. Taylor (1992) Softening of rigid polyvinyl chloride by high concentrations of aqueous solutions of methylene chloride. Special Report 92-12, USA Cold Regions Research and Engineering Laboratory, Hanover, N.H.

Vonk, M.W. (1985) Permeatie van organische verbindingen door leiding-materialen. In *Permeatie en drinkwaterleidingen*, KIWA, N.V, Nieuwegein, The Netherlands, KIWA Report 85 (In Dutch with English summary).

Vonk, M.W. (1986) Permeation of organic soil contaminants through polyethylene, polyvinylchloride, asbestos-cement and concrete water pipes. *Proceedings of the American Water Works Association Water Quality Technical Conference, 1985*, vol. 13, p. 701–714.

Appendix A: Test results.

Table A1. Weight gain (%) of PVC for various contact times in the first short-term methylene chloride study.

Activity	4	8	24	48	72	168 hours
0.0 control	-0.12	0.00	-0.36	-0.57	-0.32	-0.33
0.0 control	-0.22	0.12	-0.47	-0.67	-0.46	-0.23
0.0 control	-0.23	0.12	-0.39	-0.41	-0.34	-0.34
$\bar{X}$	-0.19	0.08	-0.41	-0.55	-0.37	-0.30
0.4	0.00	0.23	0.00	0.00	0.34	0.68
0.4	-0.11	0.33	-0.22	-0.23	0.33	0.46
0.4	0.11	0.21	-0.23	0.13	0.27	0.47
$\bar{X}$	0.00	0.26	-0.15	-0.03	0.31	0.54
0.6	1.11	2.09	2.25	5.64	4.54	11.92
0.6	0.70	1.26	2.00	4.75	6.67	12.50
0.6	1.14	0.44	2.13	0.57	7.78	9.32
$\bar{X}$	0.98	1.26	2.13	3.65	6.33	11.25
0.8	2.12	4.92	14.02	25.68	20.84	18.63
0.8	6.72	10.56	8.47	12.06	7.55	20.74
0.8	5.97	6.05	18.51	26.62	11.83	28.15
$\bar{X}$	4.94	7.18	13.67	21.45	13.41	22.51

Table A2. Weight gain (%) of PVC for various contact times in the second short-term methylene chloride study.

Activity	4	8	24	48	72	168 hours
0.0 control	0.00	0.00	0.00	0.10	0.24	0.38
0.0 control	0.00	0.00	0.00	0.00	0.22	0.42
0.0 control	0.00	0.00	0.00	0.10	0.21	0.44
0.0 control	0.00	0.00	0.00	0.09	0.34	0.47
0.0 control	0.00	0.00	0.09	0.11	0.32	0.59
$\bar{X}$	0.00	0.00	0.02	0.08	0.26	0.46
0.4	0.21	0.11	0.44	0.69	0.89	1.53
0.4	0.21	0.20	0.44	0.86	0.89	1.66
0.4	0.21	0.23	0.54	0.88	1.06	1.44
0.4	0.22	0.22	0.43	0.99	1.05	1.31
0.4	0.21	0.12	0.32	1.05	1.01	1.17
$\bar{X}$	0.21	0.18	0.43	0.90	0.98	1.42
0.6	0.91	2.02	3.35	5.34	6.95	10.40
0.6	1.09	1.67	3.49	5.48	7.61	9.14
0.6	1.23	2.00	4.02	5.65	8.61	9.32
0.6	1.01	2.40	4.41	5.57	7.58	10.47
0.6	1.18	2.02	3.77	5.42	7.96	10.46
$\bar{X}$	1.09	2.02	3.81	5.49	7.74	9.96
0.8	8.54	14.12	20.72	25.31	25.23	25.63
0.8	8.03	12.75	23.92	25.68	26.03	25.06
0.8	8.70	12.96	21.45	25.67	25.42	26.77
0.8	8.48	12.42	22.97	25.11	25.41	25.68
0.8	9.13	13.33	22.48	25.15	24.68	25.50
$\bar{X}$	8.58	13.12	22.31	25.39	25.35	25.73

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Table A3. Weight gain (%) of PVC for various contact times in the long-term methylene chloride study.

Activity	1	2	3	4	6	8	12	16	20 weeks
0.00 control	0.12	0.09	0.11	0.11	0.12	0.25	0.43	0.22	0.32
0.00 control	0.11	0.22	0.22	0.00	0.11	0.24	0.22	0.35	0.32
0.00 control	0.11	0.22	0.22	0.22	0.00	0.23	0.33	0.22	0.32
$\bar{X}$	0.11	0.18	0.19	0.11	0.08	0.24	0.33	0.26	0.32
0.05	0.11	0.21	0.30	0.28	0.33	0.34	0.35	0.47	0.45
0.05	0.11	0.23	0.39	0.20	0.22	0.22	0.33	0.44	0.43
0.05	0.11	0.11	0.21	0.33	0.22	0.32	0.43	0.45	0.44
$\bar{X}$	0.11	0.19	0.30	0.27	0.26	0.30	0.37	0.45	0.44
0.10	0.24	0.36	0.23	0.23	0.32	0.46	0.33	0.56	0.57
0.10	0.24	0.30	0.55	0.22	0.22	0.38	0.62	0.54	0.56
0.10	0.23	0.22	0.47	0.12	0.22	0.33	0.54	0.53	0.55
$\bar{X}$	0.24	0.29	0.41	0.19	0.26	0.39	0.50	0.54	0.56
0.20	0.44	0.33	0.44	0.64	0.99	0.80	0.76	1.00	1.09
0.20	0.45	0.34	0.54	0.64	0.82	0.79	0.93	0.80	1.10
0.20	0.22	0.34	0.44	0.79	0.48	0.75	0.89	1.09	1.04
$\bar{X}$	0.37	0.33	0.47	0.69	0.76	0.78	0.89	0.96	1.07
0.40	1.03	0.98	1.59	1.94	2.07	2.36	3.25	3.64	4.36
0.40	0.98	1.09	1.47	2.02	1.82	2.57	3.00	3.31	4.03
0.40	0.97	1.25	1.36	1.84	2.10	2.24	2.90	3.42	4.43
$\bar{X}$	0.99	1.11	1.48	1.93	2.00	2.39	3.05	3.46	4.27

Table A4. Weight gain (%) of PVC for various contact times in the first TCE study.

Activity	4	8	15	22	33	68 days
0.0 control	0.12	0.21	0.19	0.11	0.12	0.11
0.0 control	0.11	0.22	0.23	0.11	0.22	0.11
0.0 control	0.00	0.11	0.25	0.12	0.11	0.12
$\bar{X}$	0.08	0.18	0.22	0.11	0.15	0.12
0.2	0.00	0.10	0.36	0.11	0.11	0.23
0.2	0.11	0.24	0.11	0.19	0.12	0.22
0.2	0.11	0.22	0.21	0.21	0.11	0.24
$\bar{X}$	0.07	0.19	0.23	0.17	0.11	0.23
0.4	0.10	0.37	0.38	0.43	0.66	0.42
0.4	0.35	0.35	0.31	0.43	0.24	0.44
0.4	0.32	0.34	0.32	0.22	0.47	0.44
$\bar{X}$	0.26	0.35	0.34	0.36	0.46	0.43
0.6	0.23	0.45	0.67	0.55	0.80	0.88
0.6	0.44	0.38	0.55	0.66	0.83	0.75
0.6	0.45	0.44	0.54	0.69	0.92	0.88
$\bar{X}$	0.37	0.42	0.59	0.63	0.85	0.83
0.8	0.76	1.27	1.09	1.25	1.63	2.48
0.8	0.53	0.80	1.07	1.71	1.77	2.21
0.8	0.51	0.73	1.35	1.14	1.85	3.33
$\bar{X}$	0.60	0.93	1.17	1.36	1.75	2.68
1.0	1.41	2.07	3.40	5.07	6.68	11.70
1.0	1.46	2.04	3.22	3.92	5.98	12.06
1.0	1.60	2.25	3.00	5.22	6.56	11.15
$\bar{X}$	1.49	2.12	3.21	4.73	6.41	11.64

Table A6. Weight gain (%) of PVC for various contact times in the mixed-organic-solute study.

Treatment	2	4	7	14	21 days
control	0.23	0.12	0.11	0.28	0.22
control	0.00	0.00	0.11	0.11	0.22
control	0.11	0.00	0.22	0.00	0.22
$\overline{X}$	0.11	0.04	0.15	0.13	0.22
organic solution	11.43	9.12	5.75	18.26	14.15
organic solution	8.53	5.81	7.27	15.94	7.08
organic solution	6.29	6.06	8.60	8.46	10.33
$\overline{X}$	8.75	7.00	7.21	14.22	10.52

Table A5. Weight gain (%) of PVC for various activities in the second TCE study. Measurements were made after 11 weeks of contact time.

	0.0	0.2	0.4	0.6	0.8	1.0
	0.12	0.47	0.76	1.28	4.95	18.79
	0.11	0.33	0.56	0.97	4.21	17.56
	0.11	0.33	0.91	1.33	3.92	19.01
	0.00	0.38	0.64	0.76	4.18	18.89
	0.00	0.44	0.92	1.28	4.79	19.44
	0.00	0.47	1.09	0.92	4.23	21.00
	0.00	0.34	0.54	1.00	4.56	18.03
	0.11	0.45	0.76	1.14	4.29	18.69
	0.12	0.56	0.76	1.11	4.08	16.59
	0.11	0.35	0.57	1.05	4.43	18.10
$\overline{X}$	0.068	0.41	0.75	1.08	4.36	18.61

Table A7. Weight gain (%) of PVC for two contact times in the acetone study.

Solution concentration (%)	3	7 days
0.05	0.11	0.22
0.5	0.32	0.19
5	0.11	0.22
25	0.23	0.45
50	4.51	4.79
75	20.43	18.67

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Louise V. Parker and Thomas A. Ranney

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13. ABSTRACT (Maximum 200 words)

This research examined softening of rigid PVC by aqueous solutions of organic solvents known to be good PVC swelling agents. Significant changes in the hardness readings of rigid PVC exposed to aqueous solutions of methylene chloride (a good PVC swelling agent) occurred at thermodynamic activities as low as 0.1, which is much lower than has been reported or predicted. Rigid PVC became rubbery after exposure to 0.6-activity solutions of methylene chloride. Whether a similar phenomenon occurs with TCE, which is not as good a PVC swelling agent, is not clear from these preliminary studies.

This study also looked at the effect of a mixture of several organic solvents dissolved in an aqueous solution. A solution that contained three good PVC swelling agents, each at an activity of 0.3, rapidly softened PVC (within 2 days). This indicates that there is some type of interactive or cumulative effect associated with mixtures of organic solutes, with each solute at an activity of 0.3 or higher.

A study was also conducted to determine if aqueous solutions of a good PVC swelling agent that is also totally miscible in water (acetone) can soften PVC. After 1 week a concentration of 50% acetone softened PVC, while a 25% solution did not.

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